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Searching for a magnetic proximity effect in magnetite-carbon structures

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Abstract

In order to study a possible magnetic proximity effect in magnetite-carbon structures, we have performed magnetization measurements of graphite-magnetite composites with different mass ratios as well as the measurement of the magnetoresistance of one of them and of the magnetization of a magnetite-carbon bilayer. The overall results do not indicate the induction of bulk ferromagnetism in graphite and disordered carbon structures through their contact with magnetite.

Key words: A. Graphite, D. Magnetic properties

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1 Introduction

The possibility of magnetic ordering in metal-free carbon structures with Curie temperatures above room temperature attracts the interest of a broad spectrum of natural sciences. First systematic indications were obtained more than ten years ago by Japanese groups but without triggering the interest of the scientific community [1,2]. The ferromagnetism observed in C₆₀ polymerized in oxygen atmosphere by light[3] and by annealing at high temperatures and pressures [4,5,6], as well as in proton irradiated highly oriented pyrolytic graphite [7] provides indications for a metal-free magnetic ordering above room temperature.

Nevertheless, the influence of ferromagnetic impurities, especially that of Fe and magnetite (Fe₃O₄), has to be taken into account carefully because most

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of the carbon-based samples show relatively weak ferromagnetic signals. Measurements of the magnetization of graphite nodules from a meteorite[8] and of the magnetic force gradients of carbon nanotubes in contact with ferromagnetic substrates[9] suggest that magnetic ordering in graphite and probably in other carbon-based structures[10] might be induced by an anomalously large magnetic proximity effect. A relatively large magnetization-decay length (identical to the spin-diffusion length) $\lambda_s \approx 5$ nm was estimated for the interface graphite-magnetite [8]. Without doubt, a magnetic proximity effect in carbon structures with such a decay length would provide interesting possibilities for applications as well as trigger further theoretical and experimental work. Therefore, further systematic studies are necessary to check whether such a phenomenon exists and how large λ_s might be. The present work is a systematic approach to estimate experimentally the possible magnetization-decay length. For that purpose we have measured the magnetization of graphite-magnetite composites with different ratios of the two components and the magnetoresistance of one of them.

We note that the graphite matrix in the meteorite nodules measured in Ref. [8] is unlikely to be well ordered. The magnetoresistance of the meteorite graphite reported in Ref. [8] deviates qualitatively and quantitatively from that measured in highly oriented samples [11]. The observed square field dependence as well as the very small increase of the resistance with a field of a few tesla[8] indicate that the graphite material in the meteorite must be considered as highly disordered. Taking this into account we have tried to simulate an interface between magnetite and a highly disordered graphite material by depositing a disordered carbon film on top of a magnetite film. Within experimental errors, the results obtained for the magnetization of our samples as well as magnetoresistance measurements performed on the graphite-magnetite composites do not provide clear indication that such a large proximity effect exists. Taking into account these results we suggest other possibilities for the origin of the additional magnetization measured in the graphite nodules.

The paper is organized as follows. In the next section details on sample preparation and experimental methods are given. In section 3 we present the results with the discussion and in section 4 the conclusion with an alternative explanation for the observed ferromagnetic response of the meteorite nodule.

2 Experimental details

A magnetite film was prepared by pulsed laser deposition (PLD) from a stoichiometric polycrystalline magnetite target onto a (100) MgAl_2O_4 substrate with an area of 5×5 mm². Substrate temperature and oxygen partial pressure during deposition were 430°C and 1×10^{-5} mbar, respectively. The laser pulse

energy was 600 mJ; the film was made with 6800 laser pulses corresponding to a magnetite film thickness of $\simeq 20$ nm. After characterization of the magnetite film a carbon film was deposited onto this film by PLD in another vacuum chamber especially used for nonmagnetic materials. The deposition was performed at room temperature, in vacuum (2×10^{-5} mbar) with a laser pulse energy of 800 mJ and a repetition rate of 3 Hz. 4000 pulses were used to get a thickness of the carbon film of (15 ± 5) nm.

The composites were fabricated from commercial Fe_3O_4 and graphite powder. Both graphite (magnetic impurity content < 0.1 ppm) and magnetite powder had micron sized grains. The powders were mixed in an appropriate mass ratio in an agate mortar and afterwards pressed into pellets with radius of 5 mm and typical height of 2 mm with a typical mass of ~ 30 mg.

The magnetic moment of the samples was measured with a SQUID magnetometer (MPMS-7, Quantum Design). In case of the composites the measurements were carried out in standard DC mode. For the bilayer the measurements were performed before and after the carbon deposition using the reciprocating sample option (RSO) with a sensitivity of $\sim 10^{-10}$ Am². Resistance measurements were performed in the van der Pauw configuration [12] using a He-flow cryostat (Oxford Instruments) equipped with a 9 T superconducting solenoid. The current-voltage characteristics were linear at least up to a current of 100 mA.

3 Experimental Results and Discussion

3.1 Magnetite-Carbon Bilayer

Figure 1 shows the magnetic moment of the magnetite film alone and of the same sample after carbon deposition as a function of magnetic field by cycling the field between +1 T and -1 T at a temperature $T = 5$ K. Figures 2 and 3 show similar measurements but at $T = 300$ K. The values of the saturation magnetic moment measured at $T = 300$ K are similar within 0.4% for magnetite alone and the bilayer. At this temperature the remanence value is about 2% larger in the bilayer than in the magnetite film alone. At 5 K however, the remanence decreased after depositing the carbon film, see Fig. 1. Our experience indicates that the reproducibility of the measurements in our SQUID is within 0.5%. Therefore, the small differences in the magnetic saturation moments between Fe_3O_4 and the $\text{Fe}_3\text{O}_4/\text{C}$ bilayer are near the experimental error limit and no clear magnetic influence can be asserted to Fe_3O_4 on carbon.

Nevertheless, a maximum estimate for the penetration depth can be obtained

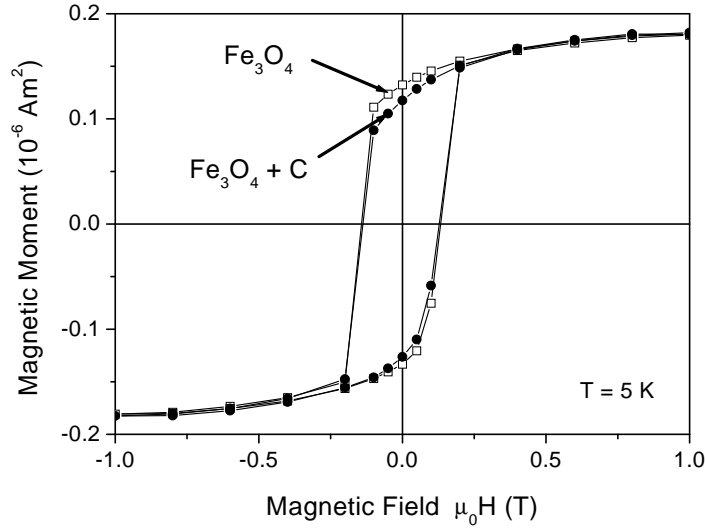


Fig. 1. The magnetic moment as a function of applied field parallel to the main area of the bilayer $\text{Fe}_3\text{O}_4\text{-C}$. Within 1% the values of the magnetic moment at $\mu_0 H = 1$ T of magnetite and of the bilayer are similar. It is noticeable that the values at lower fields $\mu_0 H < 0.2$ T are smaller for the bilayer, in the case of the remanence 5% in the negative and 12% in the positive part, as for the magnetite film without the carbon layer.

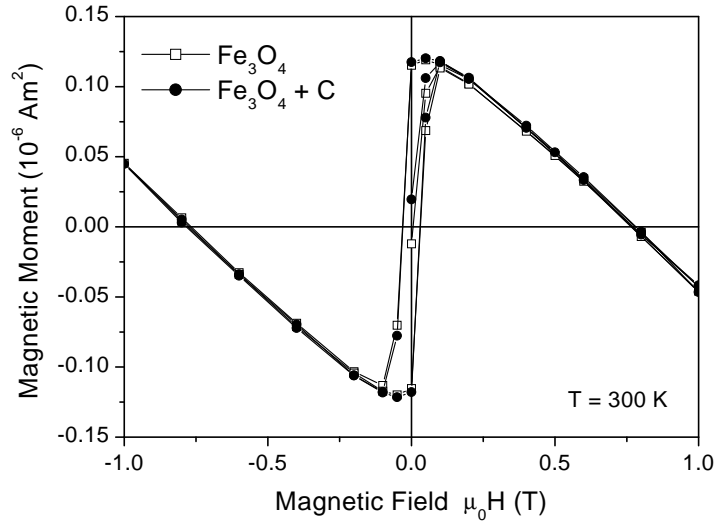


Fig. 2. Fig. 2 shows the same as Fig. 1, but for $T = 300$ K.

for the bilayer system within experimental error. The influence of the carbon layer on the magnetization of the bilayer without a proximity effect can be estimated as follows. The mass of the carbon layer for $\simeq 15$ nm thickness and a mass density of 2 g/cm^3 is $\simeq 10^{-6} \text{ g}$. The paramagnetic contribution of the carbon film[13] to the magnetic moment of the $\text{Fe}_3\text{O}_4/\text{C}$ bilayer at $\mu_0 H = 1$ T

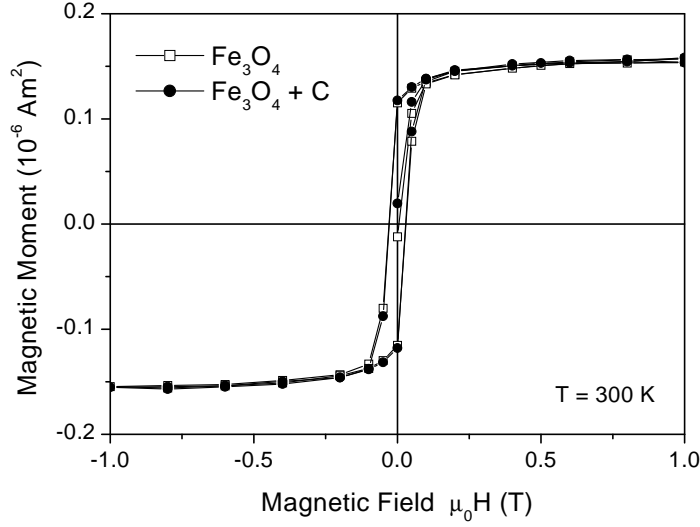


Fig. 3. Fig. 3 shows the same as Fig. 2, but after subtraction of the diamagnetic contribution from the substrate.

and $T = 5$ K is of the order $1 \dots 2 \times 10^{-7}$ emu ($1 \dots 2 \times 10^{-10}$ Am²), i.e. three orders of magnitude smaller than the corresponding value of the sample. At room temperature the contribution of the carbon layer is even smaller.

Let us assume now naively an effective magnetic penetration depth of magnetite in the carbon layer of 0.4 nm (about half of the lattice constant of magnetite) and that in this depth the carbon material shows the same magnetization as magnetite. In this case 2% of the magnetite volume is composed of carbon and the saturation magnetic moment of the bilayer would be enhanced by 2% in comparison to the single magnetite film. Within experimental error the observed maximum possible increase of the magnetization of the bilayer is 1% and 0.4% at 5 K and 300 K, respectively. In this case the observed changes in the saturation moments would correspond to effective penetration depths of 0.2 nm and 0.08 nm, respectively.

Let us assume an exponentially decaying magnetization in the carbon film of the form $M = M_0 \exp(-z/\lambda_s)$. In this case the magnetic moment in the carbon film of area A and thickness d_c is given by

$$m_{\text{carbon}} = M_0 A \int_0^{d_c} dz \exp[-z/\lambda_s] = M_0 A \lambda_s [1 - \exp(-d_c/\lambda_s)] \quad (1)$$

and the ratio of magnetic moments of the carbon and the magnetite film (thickness d_F) is

$$\frac{m_{\text{carbon}}}{m_{\text{magnetite}}} = \frac{\lambda_s}{d_F} \left[1 - \exp\left(-\frac{d_c}{\lambda_s}\right) \right]. \quad (2)$$

With $d_c = 15$ nm and $d_F = 20$ nm and from the remanence values at 300 K we may write $m_{\text{carbon}}/m_{\text{magnetite}} \leq 0.02$. From Eq. (2) we obtain an upper limit for the magnetic-diffusion length of magnetite in carbon $\lambda_s \lesssim 0.4$ nm. If the penetration depth of magnetite in carbon would be 5 nm, as assumed in Ref. [8] the enhancement would be easily measurable. This is not observed experimentally.

3.2 Magnetization of Magnetite-Graphite Composites

The magnetization curves of a pure magnetite powder compact and magnetite-graphite composites with mass ratios 1:1 and 1:10 are shown in Fig. 4. The measurements were performed at 130 K in order to work at low temperatures but above the Verwey transition of magnetite. The mass magnetization was calculated from the measured magnetic moment divided by the *magnetite weight alone*. In case of the 1:1 composite the magnetization increases $\leq 1.2\%$ at 1 T, whereas the magnetization of the 1:10 composite clearly decreases. Only a part of this decrease could be due to the inaccurate magnetite mass determination in this dilute mixture. Note that quantitatively the observed changes cannot be due to the diamagnetic contribution of the graphite powder because this shows a magnetization at 130 K of [13] $M_{\text{graphite}} = -0.01 \text{ Am}^2/\text{kg}$ and it contributes, even for the 1:10 composite, by a factor less than 1.5×10^{-3} to the total magnetic moment. Taking into account a relative accuracy of the order of 0.5% between different runs in the SQUID (measuring the same sample re-mounted in another sample holder) and a mass accuracy of 1%, the magnetization increase observed for the 1:1 composite is within experimental error. Due to the relatively large size of the magnetite grains, this experimental error is already too large to definitely rule out the existence of an anomalous large proximity effect as the estimates done below show.

We can estimate the maximum spin-diffusion length as follows. Consider a spherical magnetite particle with radius r_0 and magnetization M_0 embedded in graphite. This is assumed to induce a magnetization in the adjacent graphite of the form $M_0 \exp[-(r - r_0)/\lambda_s]$. Here the strong anisotropy of graphite is neglected such that λ_s is some orientation-averaged quantity. The magnetic moment in the graphite can be calculated to

$$m_{\text{graphite}} = 4\pi M_0 \int_{r_0}^{\infty} dr r^2 \exp[-(r - r_0)/\lambda_s] = 4\pi M_0 [r_0^2 \lambda_s + 2r_0 \lambda_s^2 + 2\lambda_s^3] \quad (3)$$

and the ratio of the magnetization of the graphite and the magnetite inclusion is then given by (for a mass ratio 1:1)

$$\frac{M_{\text{graphite}}}{M_0} = 3u [1 + 2u + 2u^2] \quad (4)$$

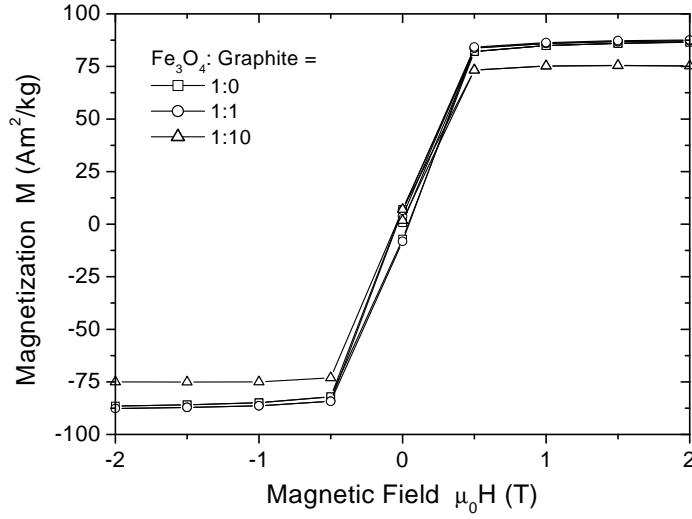


Fig. 4. Magnetization of a pure magnetite powder compact and magnetite-graphite composites with mass ratios 1:1 and 1:10. The magnetization was calculated from the measured magnetic moment by dividing through the magnetite mass alone. The measurements were carried out at 130 K.

with $u = \lambda_s/r_0$. If we assume that for the composite with mass ratio 1:1 a magnetization enhancement of 1.2%, $u \lesssim 0.004$. With a typical magnetite-particle radius of $1 \mu\text{m}$ this sets an upper limit to the spin-diffusion length of $\lambda_s \lesssim 4 \text{ nm}$. This value is within the value assumed in Ref. [8] although the experimental error does not allow a clearer statement. In the case of the 1:10 composite, the total absence of an increase in the magnetization suggests a negligible spin penetration depth of magnetite in the graphite grains.

3.3 Magnetoresistance of Magnetite-Graphite Composites

If some magnetization is induced in the graphite grains, one might expect to observe some anomalies near the coercive field in the magnetoresistance of the composite. Therefore as an additional evidence we performed magnetoresistance measurements on a magnetite-graphite composite with mass ratio 1:3. The magnetoresistance ratio is defined as

$$MR = \frac{R(H) - R(0)}{R(0)} \quad (5)$$

and it is shown in Fig. 5 for this composite. With increasing temperature the magnetoresistance decreases and the functional form changes from linear to quadratic as it is typical for graphite. An effect of the magnetite grains on the total magnetoresistance could not be detected. This becomes more evident

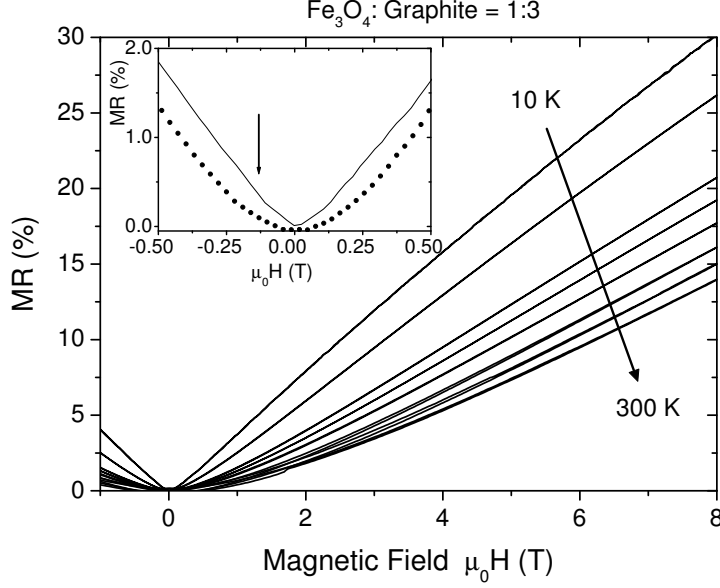


Fig. 5. Magnetoresistance ratio of a magnetite-graphite composite with mass ratio 1:3 at various temperatures, from top to bottom: 10, 50, 100, 120, 150, 200, 250, 300 K. The inset shows the magnetoresistance at 10 K (continuous line) and 200 K (points) on an expanded scale. The arrow indicates the position of the coercive field of magnetite powder at 10 K.

from the inset which shows the magnetoresistance at two temperatures on an expanded field scale.

4 Conclusion and alternative explanations

The results presented in this experimental study do not indicate a significant enhancement of the ferromagnetism induced by magnetite in bulk carbon. Although in the case of the composites of mass ratio 1:1 and because of the relatively large graphite grains embedded in a magnetite matrix (or vice versa) the experimental error does not allow to rule out completely a spin-diffusion length of the order of a few nanometers, the overall results do not seem to support this picture. It is clear that more experiments have to be done, especially using large and thin ordered-graphite - magnetite interfaces for a complete and accurate characterization of an anomalously large proximity effect. This task is however not simple due to the difficulties one has to grow one material onto the other. Recently, local ferromagnetism in C/Fe multilayers was observed by resonant magnetic reflectivity of circularly polarized synchrotron radiation [14]. The thickness of the carbon layers was 0.55 nm in comparison with 2.55 nm for the Fe-layers. Taking into account an average roughness of 0.35 nm at the interface where a mixture of C and Fe exists, the induced ferromagnetism appears within a penetration depth of less than 0.5 nm. This

result would agree with the results of Sec. 3.1 where we obtain $\lambda_s \lesssim 0.4$ nm.

The experimental data reported in Ref. [8] indicate that at least two samples from the graphite nodule do not show an enhancement of ferromagnetism in the carbon matrix, although more than 40% (in weight) graphite was in contact with almost the same mass quantity of Fe and magnetite. There is no clear reason why the proximity effect between graphite and the Fe-based ferromagnets should not apply for all the samples reported in Ref. [8]. On the other hand, those results show an inhomogeneously distributed magnetic ordering in the carbon matrix of the meteorite. Taking into account these and our results we suggest an alternative explanation for the ferromagnetism observed in the meteorite.

Previous[2] and recently published experimental work[7] indicate that hydrogen may trigger a ferromagnetic ordering in graphite. Theoretical work[15,16] suggests that a mixture of sp^2 and sp^3 carbon-hydrogen bonds may shift the spin-band structure of a graphene layer producing a 100% spin polarized band. Other theoretical work[17] indicates the existence of an extraordinarily large magnetic moment localized at a carbon vacancy position when a H atom occupies this place. Recently published work indicates that hydrogen modifies substantially the electronic structure of graphite around it. According to STM/AFM measurements [18] a single H-atom interacting with a graphite surface modifies the electronic structure over a distance of 20 to 25 lattice constants. Also, muon spin rotation/relaxation experiments [19] indicate that a positive muon (basically equivalent to a proton) in graphite triggers a local magnetic moment around it. We note further that it is highly probable that the interstellar matter studied in Ref. [8] has been naturally proton irradiated in space. Astrophysicists have speculated already some time ago that interstellar graphite and other carbon-based meteorites and dust may act as catalyst for the creation of molecular hydrogen in the universe (see Ref. [20] and Refs. therein). Therefore, the measurement of the H content of those samples and the behavior of the ferromagnetic signal as a function of high-temperature annealing time could bring light on the origin of their ferromagnetism. As a further example we refer to the ferromagnetism in polymerized fullerenes, where an inhomogeneously distributed ferromagnetic material (only $\sim 30\%$ of a ferromagnetic sample appears to be ferromagnetic), is observed by magnetic force microscopy measurements [5,6]. A defect structure added to the influence of hydrogen or other light atoms, may lead to the observed inhomogeneous magnetic ordering.

If the ferromagnetism in the graphite matrix is related neither to disorder nor to the bonding of H (or other light atom), then it may be possible that embedded Fe in the graphite matrix triggers an unusual magnetic ordering in the graphite band structure. Recent calculations of the magnetic moment of Fe atoms fixed at specific places of the graphene layer indicate a slight

decrease of its value compare to that of the free atom [21]. However, to our knowledge it appears that there is no calculations on the influence of Fe atoms on the spin distribution of the graphene layer if these reside at specific sites, e.g. at the edges or at the vacancies of the structure. Theoretical studies in this direction would be very helpful to understand the influence of magnetic ions in carbon structures. From the experimental side irradiation of graphite samples with Fe ions may provide some light on this issue. These experiments are currently being performed and their results will be published elsewhere.

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